J. of Supercritical Fluids 96 (2015) 124–132

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

High pressure in synthetic fuels production

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ARTICLE INFO

Article history:
Received 16 May 2014
Received in revised form
22 September 2014
Accepted 23 September 2014
Available online 30 September 2014

Keywords:
bioliq process
Gasification
Gas cleaning
Synthesis gas
Dimethyl ether

ABSTRACT

In regard to climate protection and saving of fossil resources, renewable and sustainable sources for energy, materials and chemicals are required. Among them, biomass is the only renewable carbon source and should be used preferentially for chemicals and materials production on a long term. Also, biomass can significantly contribute to mobility by different types of biofuels. By gasification of biomass or suitable bio-based intermediates the whole variety of today's fuels is accessible on a synthetic basis by appropriate syntheses such as Fischer–Tropsch or methanol reactions. In recent process developments, gasification, gas cleaning and conditioning and syntheses processes are conducted at elevated pressures up to 100 bar. Regarding the special features by using biomass as a feedstock, partly with high temperatures and at increased pressure a variety of specific scientific and technical questions arise along such a process chain. At the example of the bioliq® pilot project actually developed at Karlsruhe Institute of Technology (KIT) for synthetic fuels production from biomass, spotlights are provided giving insight into the manifold multidisciplinary area of high pressure research and technology in this field of research and development. In this context, high pressure aspects in gasification, gas cleaning and synthesis of dimethyl ether (DME) are presented.

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1. Introduction

Via synthesis gas, a broad range of fuels and chemicals is accessible as depicted in Fig. 1. Regarding the various possible feedstocks and potential products, syngas can be considered as a switch between energy and chemicals, but also as a common platform for use of fossil feedstocks and biomass. Synthetic biofuels, also referred to as BtL (biomass to liquids) or 2nd generation biofuels utilize lignocellulosic feedstocks. Unlike the so-called 1st generation biofuels such as bioethanol or biodiesel relying on sugar or vegetable oil containing crops, 2nd generation biofuels make use of non-edible parts of biomass. Residues and by-products from agriculture and forestry like straw or thinnings as well as feedstocks from purpose-grown energy plantations can be used. Since these materials are to be collected over wide areas and usually exhibit low volumetric energy densities, logistics of the biomass feedstock become most important for the efficiency of the overall value chain. Therefore, pre-treatment processes prior to gasification are recommended in order to obtain an intermediate fuel with increased energy density, which has to be suitable for easy transportation, storage and feeding to the gasification. Thus, pre-treatment in regionally distributed places allows supplying a large scale gasifier and synthesis plant complex with sufficient amounts of feed fuel as required by economies of scale. Central element of any synfuel production is the generation of synthesis gas (syngas) of a quality suitable for chemical synthesis, i.e. low in tar components and methane content. Depending on the synthesis process selected, the syngas requires compression up to the desired operation pressure or gasification already at elevated pressures. Example reactions are given in Table 1. Some of the reactions show a significant dependence on pressure as also indicated in the table.

To avoid syngas compression, gasification can be performed already at elevated pressures according to those required by the subsequently following synthesis process. In coal conversion to synthetic fuels and chemicals (CtL, coal to liquids) high pressure fixed bed gasifiers (FBDB^{TM} gasifiers) are in use for several decades already in South Africa (Secunda, 170,000 bbd) and also, entrained flow gasifier units up to 500 MW thermal fuel capacity (Ningxia coal-to-polypropylene plant, 5 × 500 MW) are state of the art today [1]. For GtL processes (Gas to liquids) as e.g. in Qatar (260,000 bbd) or Malaysia (Bintulu, 14,700 bbd) natural gas is reformed catalytically by partial oxidation.

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http://dx.doi.org/10.1016/j.supflu.2014.09.031
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Table 1
Reaction equation and typical process conditions of selected syngas reactions.

No.	Reaction to	Reaction equation	T (°C)	p (bar)	p-depen-dence
1	Methanol	$CO + 2H_2 \Leftrightarrow CH_3OH$	220–275	50–100	+
2	Ethanol, alcohols	$nCO + 2nH_2 \Leftrightarrow C_nH_{2n}OH + (n-1)H_2O$			+
3	Dimethylether	$2\ CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O$	∼250	∼65	O
3	Gasoline	$2\ CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O$			O
4a		$nCH_3OCH_3 + nCH_3OH \Leftrightarrow$ “$(CH_2)_{3n}$” $+ 2nH_2O$	∼350	∼20	O
4b		$nCH_3OCH_3 \Leftrightarrow$ “$(CH_2)_{2n}$” $+ nH_2O$			O
5	Fischer–Tropsch	$nCO + 2nH_2 \Leftrightarrow$ “C_nH_{2n}” $+ nH_2O$	220–340	30	+
6	Hydrogen	$CO + H_2O \Leftrightarrow CO_2 + H_2$	250–450	1–80	O
7	Methane	$CO + 3H_2 \Leftrightarrow CH_4 + H_2O$	240–600	1–100	+

Before synthesis, the syngas has to be cleaned and conditioned. Catalyst poisons, sour gases, and carbon dioxide have to be removed or decomposed and the required carbon monoxide to hydrogen ratio of the syngas has to be adjusted. Conventional solutions exist like, e.g. the Rectisol process, in which the components to be removed are absorbed in liquid solvents like methanol or amines. Dry gas cleaning processes at elevated pressures may improve process efficiency.

Using the bioliq® process for synthetic fuels and chemicals production from lignocellulosic biomass as an example, selected pressure related issues are presented and discussed in the following sections.

2. The bioliq process

The bioliq process currently under development at Karlsruhe Institute of Technology (KIT), consists of fast pyrolysis for biomass pre-treatment, high pressure entrained flow gasification for syngas generation, high pressure-high temperature gas cleaning, DME and gasoline synthesis. From fast pyrolysis, liquid pyrolysis condensates and char are obtained. The char is suspended into the liquid condensates to yield a suspension (biosyncrude) of high energy density. Liquids or slurries can more easily be fed to a gasifier and do not require an additional fluidization agent as in the case of feeding solid particles. As gasification agent, oxygen is used, which can be assisted by steam. A refractory lined cooling screen inside the gasification reactor enables so-called slagging mode operation, by which mineral components of the biomass are released from the reactor as a liquid slag. The raw syngas produced in the pilot plant at temperatures beyond 1200 °C at pressures up to 80 bar is cleaned from particles, sour gases and undesired trace components at temperatures between 500 and 800 °C by a ceramic particle filter, fixed bed sorption and a catalytic converter. After CO_2 and water removal a two stage synthesis is applied: first the syngas is converted to methanol/DME, which in turn is further reacted to gasoline with high selectivity.

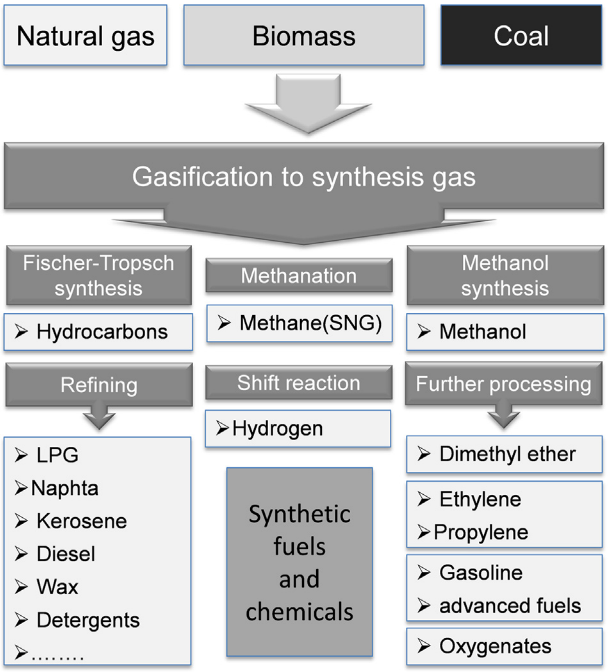

Fig. 1. Principle pathways to synthetic fuels and chemicals.

On site of KIT, a 2–5 MWth pilot plant has been erected for process demonstration and as a platform for further research and development work in regard to process improvement and optimization [2,3]. The separate process steps have been erected and commissioned in dedicated projects and full operation of the pilot plant has been achieved in 2014 for the first time. Fig. 2 shows a process scheme of the pilot plant along with trend lines for temperature and pressure regimes during the process.

3. Examples for high pressure R&D

In the following three sub-chapters, examples for pressure related research and development work related to the bioliq process are given. For gasification, atomization of the liquid-like biosyncrude is essential for proper and complete gasification to syngas (Section 3.1). Therefore, detailed knowledge on spraying processes is necessary in dependence on (i) fuel properties such as viscosity as well as particle (char and minerals contained in the biosyncrude) content and size distribution, (ii) fluid dynamics involving drop size distribution and velocity, along with (iii) operation conditions such as feed ratios, pressure, and temperature. In syngas cleaning CO_2 is currently separated by a conventional liquid solvent washing process in the bioliq pilot plant. To make this cleaning step consistent to the concept of high temperature–high pressure gas cleaning, a new process is under development utilizing solid sorption materials in combination with membrane separation (Section 3.2). Finally, the influence of pressure on the synthesis of methanol/DME has been studied in detail (Section 3.3). In the one-step DME synthesis, three reactions are to be combined in one reactor: the methanol synthesis, its dehydrogenation and the water gas-shift reaction.

3.1. High pressure spraying in gasification

Operation of a technical entrained flow gasifier aims for complete fuel conversion into a tar-free syngas at minimum oxygen consumption, i.e. maximum cold gas efficiency. To reach this goal, a fine spray should be generated at the burner nozzle. Here, the droplet size distribution has a significant influence on fuel conversion and synthesis gas quality [4]. Oxygen as a gasification agent also serves as atomization agent in the commonly applied twin fluid

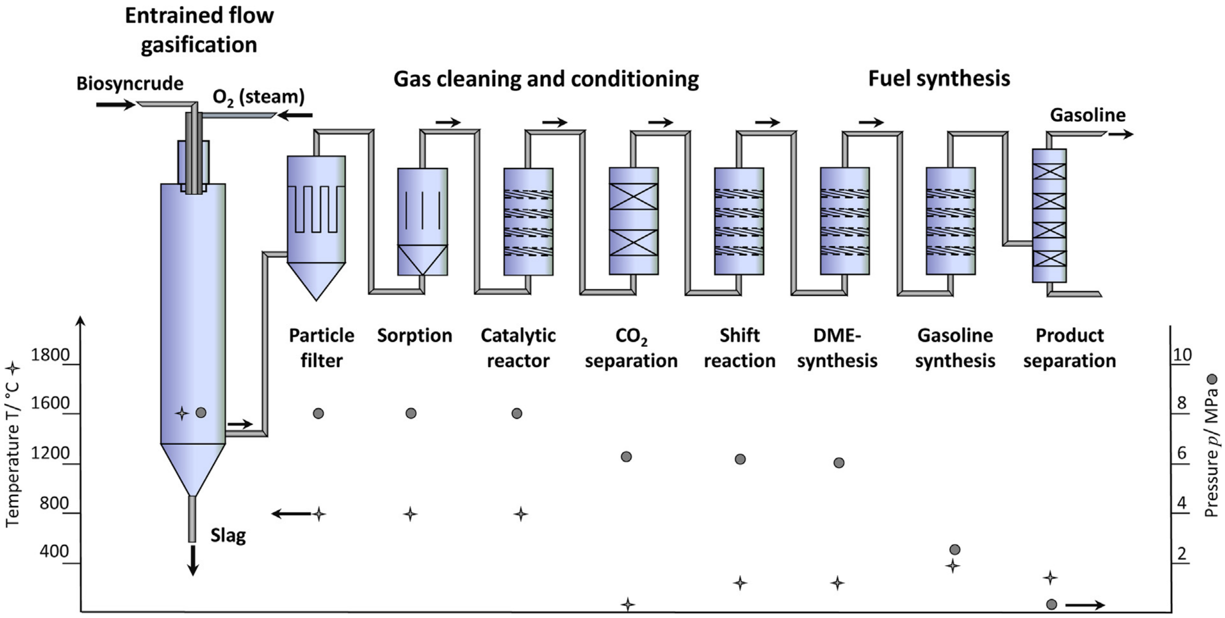

Fig. 2. Scheme of the bioliq® process along with temperature and pressure levels.

nozzles. Based on the required stoichiometry for the gasification reaction there is only a fixed, limiting amount of atomization agent available with usually low values of the gas to liquid ratio, GLR. Thus, the major challenge in nozzle design for entrained flow gasification is to produce a fine spray of the high viscous fuel suspension (biosyncrude) at low GLR and high operation pressure. For process optimization, design and scale up of the burner nozzle, fundamental knowledge concerning the atomization behavior of pumpable high viscous, non-Newtonian slurries at high process pressure is necessary. In this context, basic investigations of the effect of process pressure on the spray quality generated by a twin-fluid atomizer are carried out.

In literature numerous studies concerning twin-fluid atomization of low viscous liquids at atmospheric pressure conditions can be found [5]. Generally, detailed investigations using state-of-the-art advanced measuring techniques reported on twin-fluid atomization at elevated pressures are rather scarce. Investigations on the influence of reactor pressure on atomization of low-viscous liquids were carried out by [6–9]. Different semi-empirical correlations for Sauter mean diameter (SMD; Eq. (1)) describing the droplet size distribution in the spray were suggested. Nevertheless, the reported influence of the operational parameters on SMD from these correlations is sometimes inconsistent and in some cases even contradictory as will be demonstrated further on.

$$\mathrm{SMD} = \frac{\sum_{i=0}^{k} n_i d_i^3}{\sum_{i=0}^{k} n_i d_i^2} \tag{1}$$

Atomization at increased pressure is investigated at the *P*ressurized *A*tomization *T*est Rig (PAT) employing a twin-fluid atomizer shown in Fig. 3. Technical details of the experimental test rig can be found in [4]. To measure drop size distribution and axial droplet velocity in the spray a 2D-fiber Phase-Doppler-Anemometer (PDA) is used. The influence of operation pressure on atomization of low viscous fluids (water) was investigated by recording the local spray data for varying process parameters.

Typical semi-empirical correlations for prediction of the droplet size depending on the liquid properties and operational parameters of twin-fluid atomizers are given in literature as SMD dependency on the dimensionless Weber number (*We*, Eq. (2)) and the GLR [6–9]. Based on such correlations, the Weber number can be identified as the standard key parameter used to predict the spray quality. Therefore, the present experiments were conducted at various reactor pressures (absolute pressure 2–21 bar) keeping the aerodynamic Weber number constant.

$$We = \frac{\rho_{air} \cdot u_{relative}^2 \cdot d_{jet}}{\sigma} \tag{2}$$

with ρ_{air} being the density of air as spray environment, $u_{relative}$ the relative velocity between droplet and surrounding medium, d_{jet} a characteristic length, and σ the interfacial tension of the droplet. The obtained SMD is plotted against the reactor pressure for relatively a low *We* number ($We = 500$) in Fig. 4(a) and for a high *We* number ($We = 4000$) in Fig. 4(b). As expected, the increase in *We* number and therewith in aerodynamic forces results in a decrease of SMD at constant pressure. However, an increase in pressure at $We = \text{const.}$ leads to an increase of SMD. For comparison, the semi-empirical correlations for SMD derived in the literature [6–9] have been applied to the operational conditions used here and are also

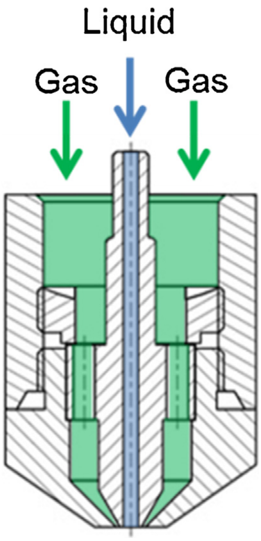

Fig. 3. Scheme of used twin-fluid atomizer.

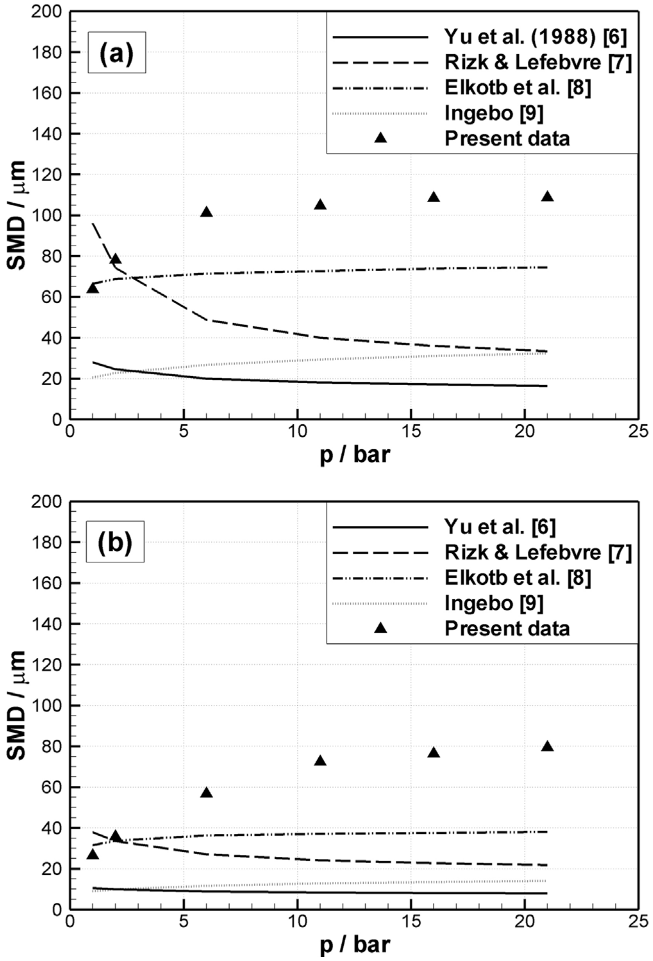

Fig. 4. (a/b) Sauter mean diameter, SMD, as function of reactor pressure and Weber number *We* of 500 (a) and 4000 (b)

shown in Fig. 4. It should be emphasized that some of those correlations have been set-up for lower reactor pressures and thus, their validity for pressures as high as 21 bar was not stated. Nevertheless it is obvious that the predicted SMD dependency on reactor pressure differs significantly for various correlations and also in comparison with the presented results. It is worth mentioning that those correlations in literature have been derived from experimental data obtained mostly at constant gas velocity determined by the relative pressure loss on the atomizer. Basically, although the correlation predictions of SMD include the *We* number their validity has not been proven for constant *We* numbers under variation of the reactor pressure. The observed increase in SMD with reactor pressure for constant *We* number seems to correlate with a strong decrease of gas velocity the dependence of which on reactor pressure can be expressed as: $u_{gas} \sim p^{-1/2}$.

Also, the primary atomization was investigated applying high speed imaging and the results are shown exemplary for the case of *We* = 500 in Fig. 5. While the primary atomization at low pressure (1 bar) is very rapid, resulting in generation of relatively small primary droplets and only minor ligament formation near to the nozzle, the liquid disintegration is delayed at high pressure (21 bar). Such a delay results in large primary ligaments that break up further downstream into droplets which are, due to the lower shear forces at this position, larger as compared to the 1 bar case.

Even though the atomization of low-viscous liquids was thoroughly investigated in the past, a surprising behavior was observed due to the rather unconventional approach of keeping the *We* number constant while varying operation pressure. This clearly illustrates that the effect of reactor pressure on twin-fluid atomization is still not well described by using semi-empirical correlations. Furthermore, the properties of the atomized fluid have a significant impact on the droplet size distribution generated at the atomizer. High fluid viscosity influences the generation of instabilities at the fluid-gas interface leading to jet disintegration as shown in the study conducted at atmospheric pressure in [10]. It was shown that the effect of viscosity is very pronounced at low GLR values as relevant for the entrained flow gasification. In general an increase of viscosity leads to larger droplets at the same operating conditions. This effect of viscosity will interfere with the effect of the reactor pressure on twin fluid atomization. Thus, the present findings clearly illustrate the need for comprehensive systematic investigations on the influence of operational parameters and also of fluid properties on twin-fluid atomization using advanced state-of-the art measuring techniques.

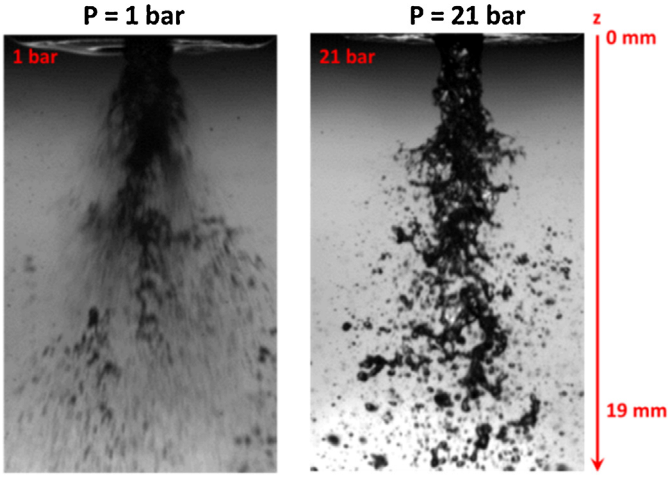

Fig. 5. Primary atomization at *We* = 500.

3.2. High temperature–high pressure CO_2 sorption

The overall efficiency of high-temperature, high-pressure (HTHP) syngas generation from high-ash biogenic feedstocks is expected to be increased significantly performing the cleaning and conditioning of the syngas also in an HTHP process. Also, the volumetric flow rate of syngas is reduced, in case the bioliq pilot plant from 700 m^3/h STP to approx. 40 m^3/h by operating at 800 °C and 80 bar instead of ambient pressure. In the context of the bioliq process, research and development work focuses on the continuous purification and conditioning of the raw syngas at operation pressures up to 80 bar and temperatures as high as possible, at maximum 800 °C, for a most effective heat recovery from the purified syngas by unproblematic heat exchange processes. In the pilot plant, a combination of different cleaning technologies consisting of ceramic filter elements, fixed bed sorption of sour gases and catalytic decomposition of undesired hydrocarbons and nitrogen containing compounds has been installed to reveal clean gas concentration levels <100 ppbv for the relevant trace contaminants particulates, S-, Cl- and N-compounds. Instead of the conventional CO_2 scrubbing by amines at low temperatures (see Fig. 2.) presently used, the further conditioning of the syngas aims at dry HTHP removal of CO_2 by an innovative approach using hydrotalcite minerals currently under development. This layered double hydroxide (LDH) enables the sorption based, selective removal of CO_2 from the pre-cleaned syngas at elevated temperatures and pressures.

Following the concept of a continuous HTHP removal of CO_2 dense ceramic membranes of such LDH minerals are currently synthesized and investigated in detail. Fig. 6 illustrates the concept of

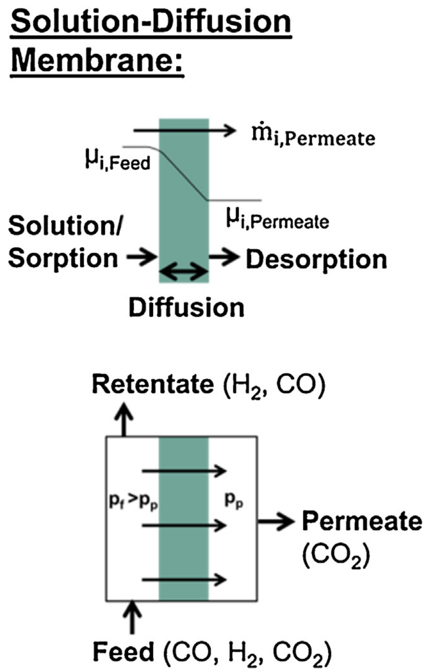

Fig. 6. Diffusion-solution membrane from hydrotalcite for continuous removal of CO_2 from synthesis gas at HTHP conditions.

the so-called diffusion-solution membrane and the basic processes involved. The separation process in the membrane is driven by the pressure differences between the feed (syngas) and the permeate (pure CO_2) only. The sorption on the syngas side, the selective diffusion through the hydrotalcite membrane and the desorption on the permeate side are the most relevant sub-steps controlling the permeation. Other dry sorbents like, e.g. CaO or Li_4SiO_4, which are also suitable for high temperature sorption of CO_2, typically require thermal regeneration with temperatures 200–300 K above sorption and calcination temperature, respectively. Likewise degradation in the long-term and attrition must be taken into account additionally [11]. The composition of the MgAl-hydroxides used here follows the general formula $[Mg_{1-x}Al_x(OH)_2]^{x+}$ for the basic structure and $[(CO_3)^{2-}{}_{x/2}\ n{\cdot}H_2O]^{x-}$ for an interlayer structure. The interlayer dimensions are controlled via the Mg/Al ratio. Optimum temperature range was identified between 400 and 500 °C. The sorption of CO_2 into the LDH structure is strongly controlled by the preceding calcination procedure as well as by sorption temperature and pressure. Moreover, the composition of the syngas and the water content influence the sorption characteristics.

Regarding the sorption step, parametric studies have been performed in lab-scale investigating the influence of calcination and sorption temperature on the sorption capacity of hydrotalcite with the molar ratio Mg/Al set to 3/1. The diagrams in Fig. 7 show the influence of pressure on sorption of CO_2 at 20, 50, and 80 bar. The calcination procedure strongly influences the sorption capacity indicating a partial change in the layered sorbent structure with the release of H_2O and CO_2 during the calcination procedure. The maximum sorption capacity is measured at 430 °C calcination temperature. At a pressure of 20 bar the sorption capacity of CO_2 is cut half to 0.4 mol/kg, when the process temperature increases from 200 to 450 °C. Data in Fig. 7 clearly show that an increase in pressure to 50 and 80 bar improves the sorption capacity of hydrotalcite at 450 °C to 0.7 and 0.9 mol/kg, respectively. The unfavorable decrease of sorption capacity with temperature in case of the untreated hydrotalcite can be eliminated completely, when the hydrotalcite is doped with potassium [12]. Fig. 8 illustrates the drastic change in the performance of the K-doped sorbent. Both, a higher calcination temperature and a higher sorption pressure strongly enhance the sorption capacity of CO_2. Optimum sorption performance is achieved at temperatures between 400 and 500 °C, where calcination of the sorbent can be done in situ. At 80 bar, CO_2 sorption of about 2 mol/kg is measured which is twice the capacity of the undoped material at the same process conditions. Moreover, the water content in the syngas doubles the maximum sorption capacity of CO_2 at 500 °C, whereas no influence of the water content was detected during the desorption procedure. Hydrotalcite prototype membranes are currently synthesized on a ceramic support and are investigated with respect to the most relevant properties such as structure, permeability and sorption selectivity in syngas mixtures.

3.3. *Influence of pressure on the direct synthesis of dimethyl ether*

In recent years, the global market for dimethyl ether (DME) is steadily growing [13]. DME can be employed as substitute for

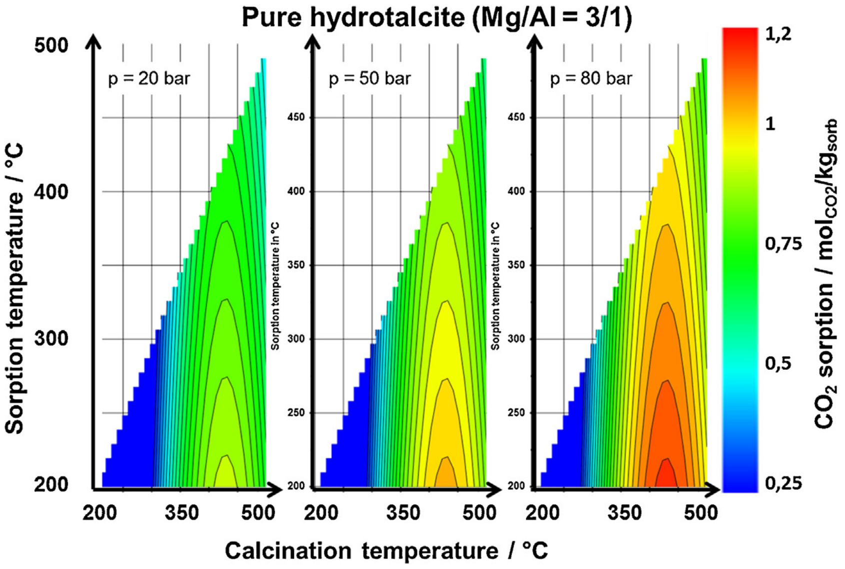

Fig. 7. Sorption of CO_2 (gas mixture 20 vol.% CO_2, 80 vol.% N_2) in untreated hydrotalcite sorbent at 20, 50, and 80 bar. Calcination temperature was always above sorption temperature.

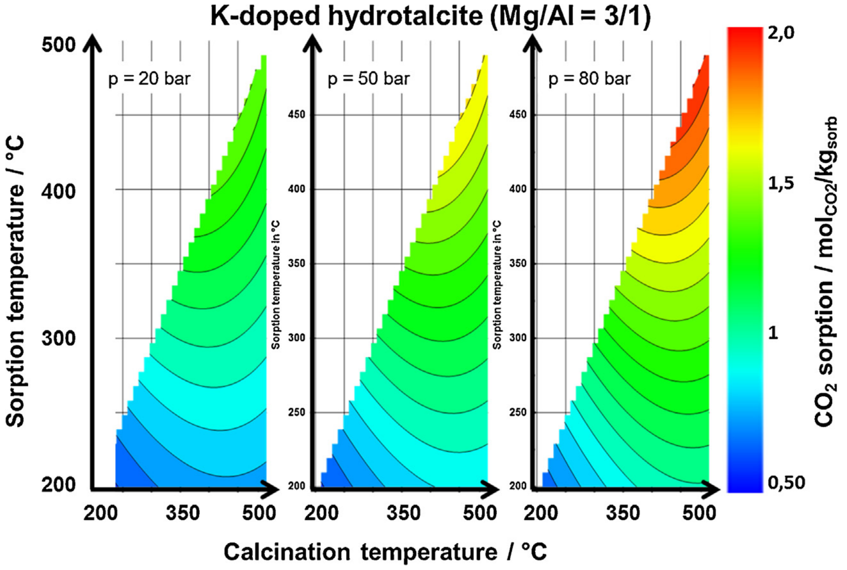

Fig. 8. Sorption of CO_2 (gas mixture 20 vol.% CO_2, 80 vol.% N_2) in K-doped hydrotalcite sorbent at 20, 50, and 80 bar. Calcination temperature was always above sorption temperature.

liquefied petrol gas or, due to its high cetane number, as a diesel substitute. Besides these direct applications, DME can also be converted to olefins or gasoline. Considering these possibilities, DME could become a future platform chemical and further developments strongly depend on the availability of highly efficient and sustainable production processes. In this context, the development of highly efficient catalysts for DME synthesis from synthesis gas plays a crucial role.

DME usually is produced in a two-step synthesis process. In a first step, methanol (MeOH) is produced which then in the second step is dehydrated to DME according to reactions 1 and 3 in Table 1. Both steps are heterogeneously catalyzed usually by a Cu/ZnO- and a γ-Al_2O_3-catalyst, respectively [14,15]. These two catalysts can also be used in one reactor, since they have roughly the same operation temperature and thus, MeOH can be converted directly further to DME. In this case, also the water gas shift reaction occurs (reaction 6 in Table 1), leading to the overall reaction equation:

$$CO + 3H_2 \Leftrightarrow CH_3OCH_3 + CO_2$$

In contrast to natural gas reforming, biomass gasification usually leads to carbon monoxide-rich syngas with $CO{:}H_2$ ratios of around one, so that direct DME synthesis appears to be attractive, which is accompanied by a strong volume contraction. High pressures should favor CO-conversion and hence, DME synthesis, according to Le Chatelier's principle. Moreover, the overall reaction is strongly exothermic ($\Delta_r H = -246.2$ kJ/mol) which results in an increase of CO-conversion with decreasing temperature. In the technical process the removal of the released heat poses therefore a main challenge in reaction engineering.

For the MeOH-synthesis the equilibrium conversion of CO at different pressures is displayed in Fig. 9 (left side). It can be seen that high pressures are required to achieve a reasonable conversion of CO. For a technical process this also implies that non-reacted syngas has to be recycled and fed to the catalyst again. This results in a large recycle stream of syngas and thus considerable demand of energy for recompressing. In current industrial processes for MeOH synthesis the ratio from fresh syngas to recycled syngas is between 1:2 and 1:8 [16]. For the MeOH-dehydration the equilibrium conversion is independent of pressure since there is no change in the mole number during the reaction. Because the reaction is slightly exothermic, high conversion at low temperatures is favored. Since the thermodynamics for both steps are favorable in the same temperature interval it is possible to use a physical mixture of both catalysts and therefore combine both steps in one reactor. Here the water-gas-shift reaction plays an important role (reaction 6 in Table 1). The water produced by the in situ dehydration of MeOH is consumed by CO to produce additional H_2 and CO_2. If the water is constantly removed from the reactor, the equilibrium of reaction 3 is shifted toward the product side, resulting in a high conversion of CO as shown in Fig. 9 (right side) in dependence of temperature and pressure. In the relevant range of temperatures the influence of pressure is very strong. For example at 275 °C the CO-conversion rises from 1.5% at 1 bar to 47% at 10 bar. This influence declines with increasing pressure; a rise from 50 to 100 bar at 275 °C results in an increase of CO-conversion of only 7%.

In recent tests, the effect of pressure on the single-step DME synthesis was studied to determine whether its influence was related to an alteration of residence time and concentration or whether the chemical reaction changed itself. Reactions were carried out in a fixed bed reactor with a length of 30 cm and a diameter of 1.6 cm. A catalyst mixture comprising 1 g each of a catalyst for methanol synthesis (commercially available $CuO/ZnO/Al_2O_3$ catalyst) and a catalyst for methanol dehydration (γ-Al_2O_3) was employed. After reduction of the methanol catalyst with H_2, the pressure was set to the respective value and the temperature to 250 °C. The total flow rate was 100 ml/min employing a gas mixture $(H_2 + CO){:}(Ar + N_2)$ with a ratio of 3:7. The $H_2{:}CO$-ratio was 1:1 and the $Ar{:}N_2$-ratio was 6:1. The dosage of gases in the laboratory plant was monitored by mass flow controllers, analysis of the gas phase was carried out using an HP 6890 gas chromatograph from Agilent which contained two columns (RT®-U-BOND and RT-Msieve 5A, both from RESTEK) and two detectors (TCD and FID). For calculating conversions and selectivities, Eqs. (3)–(5) were applied.

$$X_{CO} = \frac{(c_{CO,0} - c_{CO})}{c_{CO,0}} \times 100 \tag{3}$$

with X_{CO} being the CO conversion, $c_{CO,0}$ the CO concentration at reactor inlet, and c_{CO} the CO concentration at reactor outlet, all given in percent.

$$S_i = \frac{\xi_i \cdot c_i}{(c_{CO,0} - c_{CO})} \times 100 \tag{4}$$

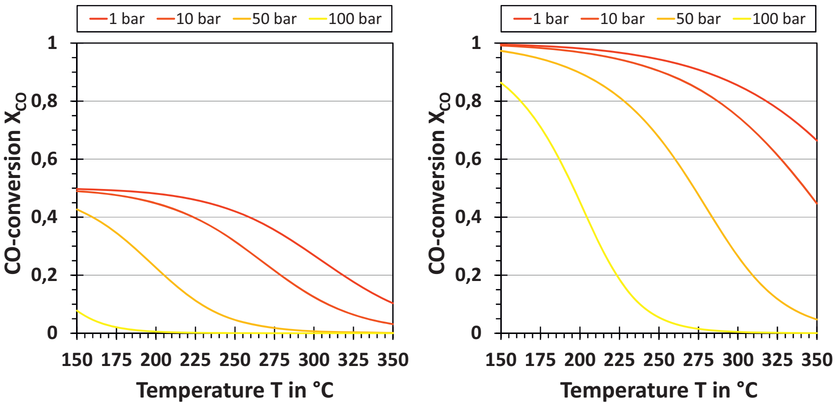

Fig. 9. Equilibrium conversion of CO for the synthesis of MeOH (left side) and for the single-step synthesis of DME (right side); H_2/CO = 1:1, components for DME (CO, CO_2, MeOH, DME, H_2, H_2O), components considered for MeOH (CO, MeOH, H_2, H_2O).

or

$$S_i = \frac{\xi_i \cdot (c_i - c_{i,0})}{(c_{CO,0} - c_{CO})} \times 100 \tag{5}$$

with S_i as selectivity of component i, $c_{i,0}$ as concentration of component i at reactor inlet, c_i as concentration of component i at reactor outlet, and ξ_i as amount of carbon atoms in component i, all given in percent.

CO conversions and DME selectivities were determined at different pressures while the other reaction parameters were kept constant (Fig. 10). CO-conversion increases with increasing pressure parallel to the corresponding, calculated equilibrium data in agreement with Le Chatelier's principle. Moreover, DME-selectivity remains constant around 69% and was not affected by pressure variation in the interval between 21 and 81 bar. In fact, even changing the H_2/CO ratio does not change the selectivity, but syngas conversion [17]. The main by-product of the reaction is CO_2 and the percentage of other by-products is found to be below 2%. These results lead to the conclusion that pressure variation can be understood as a modification of residence time. To confirm this assumption the adjusted pressures were converted into the corresponding residence times using Eq. (6) and the ideal gas law.

$$\tau_{mod} = \frac{V_{bulk,catalyst}}{\dot{V}_{total,reactor}} \tag{6}$$

with $V_{bulk,catalyst}$ as catalyst bulk volume and $\dot{V}_{total,reactor}$ as the total flow rate under reaction conditions.

In Fig. 11 the obtained data are compared to residence times, which have been adjusted by experimental variation of the gas flow rate. Within the experimental uncertainty both curves are identical. A variation of pressure changes the contact time between syngas feed and catalyst and has no influence on the chemistry of the process itself. As a result, certain flexibilities for the operation of a plant and process chain are provided. Desired pressures (and thus conversion) can be adjusted by changing the residence time and vice versa. This can help to improve operational stability and control.

4. Perspectives and future trends

The examples presented above clearly show that pressure effects are important to consider in synthetic biofuels production processes as pressure influences not only the thermodynamics, chemical kinetics, mass and heat transport properties but also the process equipment and materials to be selected.

In synfuel production the application of pressure aims at:

- Higher specific throughput relevant to plant size and capacity, but also to equipment design and purchase costs. As an example, a cost comparison of SNG (substitute natural gas) production by coal gasification at 30 and 90 bar lead to savings in investment and specific production costs by around 10% in the high pressure case [18], basing on a design capacity of 3 Mio.t of coal per year. The reason was mainly attributed to the higher thermal efficiency of gasification at higher pressure. Also, the gas volume flow

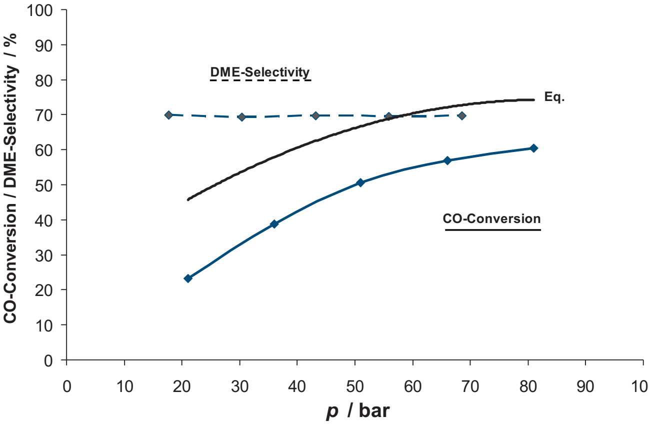

Fig. 10. Influence of pressure on CO-conversion and DME-selectivity at H_2/CO = 1 (Eq. = calculated equilibrium data).

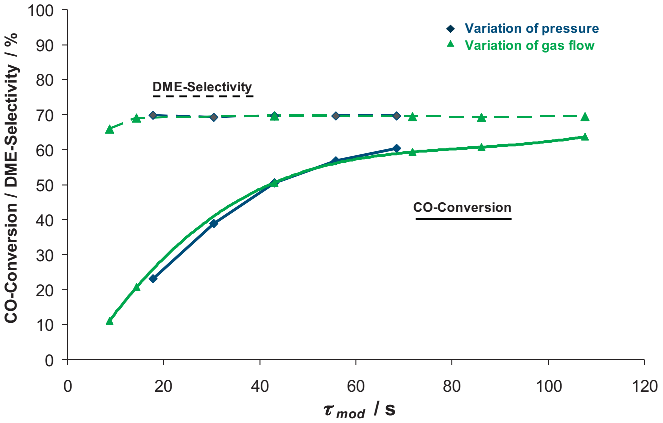

Fig. 11. Influence of pressure and gas flow variation on CO-conversion and DME-selectivity at H_2/CO = 1.

rate to be treated in gas cleaning and conditioning is reduced as mentioned in Section 3.2.
- Improved reaction kinetics and thermodynamics, mass and heat transfer properties, as shown for the higher conversion of syngas in case of DME formation. Also, selectivity or product yield, e.g. for methane production from syngas production, can be increased. In the example for SNG production given above, the methane content in the raw syngas was increased from 9.9 to 17.1 vol.% when rising pressure from 30 to 90 bar. The overall process efficiency to produce a gas with 90 vol.% of methane was increased from 60.8 to 68.6% at the same time [18].
- Saving the efforts of syngas compression before subsequent use in synthesis reactions, when liquid feedstocks are utilized for gasification. Compression of such a fuel before gasification requires much less energy than compression of the produced syngas downstream.

Application of pressure in this context is a key to improve process intensification. The goal is not the expansion of the pressure range, but to employ pressure effects to increase the efficiency of single process steps and that of the overall process in order to improve product quality and to reduce specific investment costs. This is important for two reasons. On the one hand, the production of synthetic fuels and chemicals today is not competitive to the use of fossil resources. On the basis of production sites of comparable product capacity a major concern is seen in the supply costs of sustainable biomass to industrial scale production facilities. Another approach aims at the development of smaller scale, modular facilities, able for de-centralized production of fuels and chemicals. Examples are the reforming of oils (or vapors) from fast pyrolysis or hydrothermal liquefaction to syngas and/or their upgrading to fuel grade products for use in heat and power generation or for co-refining with crude oil. In such a plant, the feedstock supply costs are expected to be lower (due to more convenient logistics for biomass provision). However, the higher specific investments are less favorable because economy-of-scale reasons compared to large industrial plants. In both cases, process intensification helps to improve economics. For the same reason product quality and thus value added to the process should be increased. As an example, the use of micro-structured reactor components is worth of mention here which are capable to withstand pressure in the order of 10^3 bar. Due to their high surface to volume ratio, selectivity can be increased compared to conventional reactor types by making use of the special heat and mass transport properties. They are particularly suited for exothermic reactions at increased pressure; e.g. in a Fischer–Tropsch synthesis at 30 bar 920 kW/m^3 of reaction heat can be released in an optimized micro-reactor, compared to a conventional slurry reactor with 11 kW/m^3 [19].

Therefore, the detailed investigation of these effects and the underlying fundaments provide an important basis for successful development, implementation, and optimization of processes for synthetic fuels and chemicals production from biomass. Considering the three most important pressure effects given above, it becomes clear that for synthetic fuels production mainly the process chain gasification–gas cleaning–synthesis takes advantage of pressure application. The pre-processing step to convert biomass via pyrolysis, torrefaction or other processes to solid and liquid intermediates, most likely cannot benefit from pressure so easily because of unpleasant handling of solid material up- and downstream the process and a lack of significant improvement options by pressure application [1]. On the other hand these processes require substantial research work on biomass specific issues, while for gasification and the subsequently following processes a considerable state-of-the-art has already been achieved by coal and natural gas conversion. However, also theses processes have to be adapted to biomass-specific issues, unless purified syngas is obtained.

Pressure related issues are not only relevant to the bioliq process but also to many other types of high pressure processes utilized in syngas production and conversion. From different biomass pretreatment processes solid and liquid intermediate energy carriers are obtained, which have to be fed into a pressurized gasifier. Thus, fuel preparation and high pressure feeding is already a first important issue. Then, different types of high pressure gasification reactors exist: entrained flow reactors as developed by Shell, Siemens, Linde, or ThyssenKrupp Uhde as well as fluid bed (Foster Wheeler, ThyssenKruspp Uhde) or fixed bed reactors (Air Liquide), all with their specific requirements related to operation at elevated pressures. For biomass conversion, these reactors are not state of the art today. Technology readiness levels from pilot to demonstration (TRL 6–7) status have been attained so far, requiring further research and development work on optimization and further process development. Conventional gas cleaning processes can be considered as state of the art; however, new developments as high temperature–high pressure gas cleaning and conditioning is also in the development phase. Processes such as Fischer–Tropsch for hydrocarbons production and methanol synthesis are also well known and operated in large scale basing on syngas produced from coal and natural gas. Regarding biomass as a feedstock, new product routes are desirable; allowing to maintain oxygen molecules in the final products, as it is already naturally contained in the biomass feedstock. By that, the energetic and carbon efficiency would be increased. Examples are high performance fuel components or additives, oxygen containing monomers for polymers (polyoxymethylene) and a broad range of fine chemicals.

There is no doubt, that syngas based processes will play an important role in the future carbon utilization. As already stated before, biomass is the only renewable carbon source. All other renewable resources can be employed for heat and electrical power production and will be increasingly used for this purpose in future energy supply scenarios. Then, biomass can be used for chemicals and fuels production instead of mainly heat and some power production as pre-dominant today. As an example, in Germany biomass presently contributes to around 70% to the challenging renewable energy targets mainly by domestic heat provision. However, carbon containing products will continue to form the basis of chemicals and liquid fuels for the next decades. On the background of climate change considerations by CO_2 emissions from fossil fuels, and on expected cost development of fossil resources due to limited availability (due to market) and exhausting resources on a longer term, the use of biomass will become more and more important. Syngas production from biomass by gasification allows for use of a broad variety of biomass types, which are not suitable for other processes. Residues from agriculture, forestry and land cultivation form an enormous mass potential fitting to the order of magnitude relevant to chemical industry and able, to contribute substantially to fuel production together with the still required first generation biofuels like biodiesel from vegetable oils and bioethanol from sugar fermentation. Therefore, syngas and synfuel production will become complementary pieces in the highly diverse and competitive puzzle of utilizing biomass to produce food and feed, construction materials, fibers, chemicals and energy.

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